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## JAPANESE / ENGLISH TRANSLATION OF

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Polyester Resin Composition for Use in Calendering

Your Ref: No. 1720

For: Eastman Chemical Company

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9109 Eagle Hills Dr . Las Vegas NV 89134 . ph: 866-722-7990 (toll-free) . fax: 702-973-6009 . email: sales@tls-translations.com

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(21) Application No.:	11-109505	(71) Applicant: 000000550 Okamoto Industries Incorporated 27-12 Hongo 3-chome, Bunkyo-ku, Tokyo
(22) Date of Filing:	16 April 1999	(71) Applicant: 591273041 Daikyo Kasei Kogyo Co., Ltd. 23-27 Toneri 5-chome, Adachi-ku, Tokyo
		(72) Inventor: Akio INABA c/o Okamoto Industries Incorporated 1 Kando, Yoshida-cho, Haibara-gun Shizuoka Prefecture
		(74) Agent: 100089406 Hiroshi Tanaka, Patent Attorney (and two others)

(Continued on last page)

**(54) [Title of the Invention]**

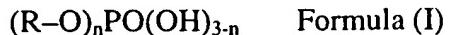
Polyester Resin Composition for Use in  
Calendering

**(57) [Summary]**

**[Object]** To provide an amorphous random polyester resin-based composition that is suited for use in calendering.

**[Means of Achievement]** A polyester resin composition for use in calendering is formed as a result of adding at least 0.01 to 5.0 wt parts of a phosphate ester-based lubricant expressed by Formula (I) below to 100 wt parts of an amorphous random copolyester resin that has a glass

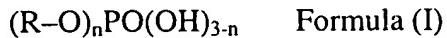
transition point of 40 to 150°C and that contains at least 80 mol% repeating units derived from an aromatic dicarboxylic acid having 8 to 14 carbons.



(In the formula,  $n$  is the integer one or two; and R is an alkyl group, alkylphenyl group, alkylpolyoxyethylene group, or alkylphenyl polyoxyethylene group.)

### [Claims]

**[Claim 1]** A polyester resin composition for use in calendering is formed as a result of adding at least 0.01 to 5.0 wt parts of a phosphate ester-based lubricant expressed by Formula (I) below to 100 wt parts of an amorphous random copolyester resin that has a glass transition point of 40 to 150°C and that contains at least 80 mol% repeating units derived from an aromatic dicarboxylic acid having 8 to 14 carbons.



(In the formula,  $n$  is the integer one or two; and R is an alkyl group, alkylphenyl group, alkylpolyoxyethylene group, or alkylphenyl polyoxyethylene group.)

**[Claim 2]** The polyester resin composition according to Claim 1, characterized in that the amorphous random copolyester resin that is used essentially comprises repeating units of 60 to 75 mol% terephthalic acid and ethylene glycol, and 40 to 25[mol]% of 1,4-cyclohexane dimethanol.

**[Claim 3]** The polyester resin composition according to Claim 1 or 2, characterized in that a mixture containing a phosphate monoester and phosphate diester in a ratio of 10:1 to 1:10 is used as the phosphate ester-based lubricant.

**[Claim 4]** The polyester resin composition according to Claim 1, 2, or 3, characterized in that 0.05 to 5.0 wt parts low- and/or high-density oxidation-type polyethylene wax is added to 100 wt parts of the amorphous random copolyester resin.

### [Detailed Description of the Invention]

#### [0001]

**[Technical Field of the Invention]** The present invention relates to a polyester resin composition for use in calendering that comprises adding at least 0.01 to 5.0 wt parts of the

aforementioned phosphoric ester-based lubricant expressed by Formula (I) to 100 wt parts of the amorphous random copolyester-based resin.

[0002]

**[Prior Art]** Research on polyester resins continues to focus on changing their chemical structure and, specifically, on altering their workability and product characteristics, such as plasticity and thermal shrinkage characteristics, as a result of making these resins into copolymers. An example of such research includes attempts aimed at, e.g., partially substituting the terephthalic acid or glycol in PET with another component to produce a random copolymer, and thereby modifying the characteristics of the polyester resin to make it suitable for a variety of applications. For example, it has been proposed to modify plasticity, adhesiveness, and other characteristics as a result of changing crystalline properties to amorphous properties, and relevant examples in the literature include improving the aforementioned adhesiveness to facilitate the manufacture of laminated products, and also improving the flexibility and thermal stability of the resulting product. Other proposals have also been made for using the aforementioned copolyester and selecting combinations of a variety of additives, e.g., specific plasticizers, to improve the adhesiveness, thermal-shrinkage, and other characteristics of the final product. Methods comprising extrusion molding and subsequent stretching have been employed in order to manufacture films or other products using the polyester resins resulting from any of the aforementioned techniques and using compositions in which an additive has been combined with the aforementioned polyester resins; however, there have been no reports relating to the use of calendering methods, which are used in the manufacture of polyvinyl chloride films and the like, as a means for molding the aforementioned polyester resins or the aforementioned resin-based compositions.

[0003] Lubricants have been extensively used for improving the moldability of plastics. Examples of the aforementioned lubricants include compounds based on metallic soaps, hydrocarbon-based low-molecular-weight polyethylenes, low-molecular-weight stearates as esters of lower alcohols and stearic acid, high-molecular-weight stearates as esters of higher alcohols and stearic acid, and acrylic acid polymers; however, the effect of lubricants obtained from combining these compounds with random copolyester resins has not been satisfactory. Furthermore, technical problems arise even when a lubricative effect is obtained; e.g., considerable deterioration in the gelling property and transparency, the incidence of blooming

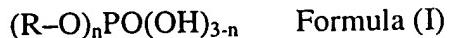
(bleeding) on the surface of the sheet over time, and the occurrence of plate-out on the calender surface. None of the lubricants that have been discovered effectively improve the calenderability of the aforementioned polyester resin compositions. Copolyesters in which 25 to 40 mol% 1,4-cyclohexane dimethanol is used for a part of the glycol component are amorphous, and films obtained using such polyester resins are known to have exceptional moldability, thermal shrinkage, and other characteristics; however, extrusion has been the process that has been adopted in the manufacture of these films, with no techniques involving calendering having been disclosed.

[0004]

**[Problems to Be Resolved by the Invention]** It is an object of the present invention to provide an amorphous random polyester resin-based composition that exhibits exceptional calenderability while retaining its gelling properties and transparency, and does not suffer from problems such as plate-out during processing or blooming/bleeding over time.

[0005]

**[Means Used to Solve the Above-Mentioned Problems]** The main point of the present invention is a polyester resin composition for use in calendering formed as a result of adding at least 0.01 to 5.0 wt parts of a phosphate ester-based lubricant expressed by Formula (I) to 100 wt parts of an amorphous random copolyester resin that has a glass transition point of 40 to 150°C and that contains at least 80 mol% repeating units derived from an aromatic dicarboxylic acid having 8 to 14 carbons.



(In the formula,  $n$  is the integer one or two; and R is an alkyl group, alkylphenyl group, alkylpolyoxyethylene group, or alkylphenyl polyoxyethylene group.) The resin is preferably a polyester resin composition characterized in that the amorphous random copolyester resin that is used essentially comprises repeating units of 60 to 75 mol% terephthalic acid and ethylene glycol, and 40 to 25% of 1,4-cyclohexane dimethanol; is more preferably the a polyester resin composition characterized in that a mixture containing a phosphate monoester and phosphate diester in a ratio of 10:1 to 1:10 is used as the aforementioned phosphate ester-based lubricant; and is ideally a polyester resin composition characterized in that 0.05 to 5.0 wt parts low- and/or

high-density oxidation-type polyethylene wax is added to 100 wt parts of the amorphous random copolyester resin. The present inventors achieved the aforementioned object of the invention in the present application by discovering as a result of trial and error that in a majority of cases where a variety of lubricants were added to an amorphous random copolyester resin, satisfactory calenderability was unexpectedly obtained when the resin was combined with a phosphate ester-based lubricant expressed by Formula (I), which had not been studied as a lubricant.

[0006]

**[Embodiments of the Invention]** The present invention shall be explained in detail hereunder. Random copolymers are preferred as polyesters used for manufacturing the copolyester resin composition used in the present invention. Although completely amorphous polyester is preferred, it is possible to use one in which some crystallinity remains but which is ordinarily deemed to be amorphous. Specific information on the random copolyester is provided hereunder.

1. Examples of polycarboxylic acids used in the manufacture of such polyesters include terephthalic acid, orthophthalic acid, isophthalic acid, sodium sulfoisophthalate, 2,6-naphthalene dicarboxylic acid, 2,6-naphthalene dimethylene carboxylic acid, paraphenylene dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, cyclohexane diacetate, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid, and other dicarboxylic acids; trimellitic acid and other tricarboxylic acids; and pyromellitic acid and other tetra-carboxylic acids. One or more of these carboxylic acids may be used. Preferred polycarboxylic acids include a combination of terephthalic acid and isophthalic acid or 2,6-naphthalene dimethylene carboxylic acid. Carboxylic acids with three or more carboxyl groups comprise an amount of approximately 0.5 mol%. It is understood that acid anhydrides, esters, and acid chlorides corresponding to the aforementioned carboxylic acids may also be used.

[0007] 2. Examples of polyhydric alcohols include ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, diethylene glycol, triethylene glycol, polyethylene glycol (up to a degree of polymerization of approximately five), polytetramethylene glycol, 2,2-dimethyl trimethylene glycol, hexamethylene glycol, *p*-xylene glycol, 1,4-cyclohexane dimethanol, neopentyl glycol, and other aliphatic/alicyclic diols; ethylene oxide adducts of bisphenol A or other dihydric alcohols; and trimethylol propane, pentaerythritol, and other tri- or tetrahydric alcohols. Alcohols having three or more hydroxy groups desirably comprise an amount of 0.5 mol% because of considerations related to the moldability of the

resulting polyester. Combinations of ethylene glycol and 1,4-cyclohexane dimethanol are preferably used as polyhydric alcohols.

[0008] Numerous examples of polycarboxylic acids and polyhydric alcohols have been provided in the foregoing, but amorphous copolymers are obtained through the combined use of terephthalic acid with a component that is used for reducing the crystallinity of the polyester, such as isophthalic acid or 2,6-naphthalene dimethylene carboxylic acid as a polycarboxylic acid. In the process, ethylene glycol or 1,4-cyclohexane dimethanol (CHDM) may be used singly as a diol component. Alternatively, amorphous copolymers may be obtained by means of using ethylene glycol together with 1,4-cyclohexane dimethanol (CHDM) as the diol component in order to reduce crystallinity. It is especially preferable to use "PETG 6763" (Eastman Chemical Co.) or another amorphous random copolyester resin in which terephthalic acid is used as an aromatic dicarboxylic acid, and 60 to 75 mol% ethylene glycol and 40 to 25 mol% 1,4-cyclohexane dimethanol (CHDM) are used as a diol. It is important in all circumstances that any property-enhancement technique that involves copolymerizing the aforementioned polyester involve adding ester units derived from terephthalic acid as the polycarboxylic acid in order to allow industrially suitable copolymers to be designed. If the glass transition temperature is 40°C or lower, the resin will become sticky, while if the temperature is 150°C or higher, the resin will become crystalline and have a high softening temperature, with neither of these ranges being suitable for calendering.

[0009] The aforementioned lubricants have conventionally been used for plastics, but when an examination was made into the characteristics of lubricants comprising mixtures in which conventional lubricants are combined with the lubricant expressed by Formula (I), which is used in the present invention, it was confirmed that low- and high-density oxidation-type polyethylene waxes (partially oxidized polyethylenes having an acid number of 1 to 40 mgKOH/g and an average molecular weight of 10000 or less) enhanced the effect of the lubricant expressed by the aforementioned Formula (I). 0.01 to 5.0 wt parts of the aforementioned polyethylene wax is preferably compounded with 100 wt parts of the amorphous random copolyester-based resin, especially when the transparency of the resulting films is taken into consideration.

[0010] Alkyl groups having 6 to 20 carbons can be cited as examples of the alkyl groups designated by R in the lubricant expressed by Formula (I), as well as the alkyl groups of the alkyl phenyl groups; examples of the alkyl groups in the alkyl polyoxyethylene groups and alkyl-

phenyl polyoxyethylene groups include alkyl groups having 6 to 20 carbons, and particularly alkyl groups having nine or more carbons; and examples of polyoxyethylenes include polymers in which two or more oxyethylene units have been added. The amount of Compound (I) to be compounded per 100 wt parts of the amorphous random copolyester-based resin is preferably 0.01 to 5.0 wt parts, and ideally 0.05 to 2.0 wt parts. An amount of less than<sup>\*</sup> 0.01 wt parts will render the effect of the lubricant inadequate, while compounding more than 5.0 wt parts will hasten the occurrence of plate-out during processing, blooming/bleeding over time, and deterioration in the transparency and other attributes of the resulting film.

[0011] The polyester resin composition of the present invention may contain a well-known additive that is conventionally used to improve the characteristics of the polyester resin product, provided that the amount does not cause a deterioration in calenderability. Examples include antioxidants based on hindered phenols, thioethers or the like; weathering agents based on benzophenones, benzotriazoles, hindered amines, or the like; epoxy compounds, isocyanate compounds, and other thickeners; dyestuffs, pigments, and other colorants; titanium oxide, carbon black, and other UV blockers; glass fiber, carbon fiber, potassium titanate fiber, and other reinforcers; silica, clay, calcium carbonate, barium sulfate, glass beads, talc, and other fillers; flame retardants; plasticizers; foaming agents; fluorescence agents; fungicidal/antimicrobial agents; crosslinking agents; and surfactants.

## [0012]

### [Working Examples] Working Example 1

The table shows a comparison of the transparency exhibited by 0.4 mm sheets obtained as a result of adding 0.5 wt parts respectively of the compounds used in Working Examples 1 through 5 and Comparative Examples *a* through *f* to 100 wt parts of a completely amorphous random copolyester resin (Eastman Chemical Co.; PETG 6763), gelling the mixtures using six-inch test rolls adjusted to a temperature of 185 to 190°C, and kneading the resulting gels for three minutes. The same compositions were also kneaded for 30 min under the same conditions, and measurements were taken of the degree of roll release lubricity, gelling time, plate-out characteristics, and sticking time. In Working Example 6, 0.3 wt parts high-density oxidation-

\* [Translator's note: the Japanese actually says "equal to or less than" here, but the range given in the previous sentence is 0.01 to 5.0, which is presumably inclusive, and accordingly the rendering of "equal to or less than" would be partially

type polyethylene wax (acid number: 16 mgKOH/g; number-average molecular weight: 5000) and 0.3 wt parts of Synthesis Product 1 below were compounded with 100 wt parts of a completely amorphous random copolyester-based resin (Eastman Chemical Co.; PETG 6763).

[0013] The compounds added as lubricants in the table are described hereunder.

Compounds used in Synthesis Products 1 through 5:

1. Monostearyl phosphate and distearyl phosphate (weight ratio: 6:4); mixed compound (AX-518; manufactured by Daikyo Kasei Kogyo Co., Ltd.).
2. Monostearyl phosphate and distearyl phosphate (weight ratio: 1:2); mixed compound
3. Monolauryl phosphate and dilauryl phosphate (weight ratio: 2:1); mixed compound
4. Monononylphenyl polyoxyethylene (number of added mols: 6) phosphate, and dinonylphenyl polyoxyethylene (number of added mols: 6) phosphate (weight ratio: 1:1); mixed compound
5. Monolauryl polyoxyethylene (number of added mols: 6) phosphate, and dilauryl polyoxyethylene (number of added mols: 6) phosphate (weight ratio: 1:1); mixed compound

[0014] Compounds of Comparative Examples *a* through *f*:

- a. Monostearyl glyceride  
(Rikemal S-100; Riken Vitamin)
- b. Low-molecular-weight polyethylene wax  
(Hi-wax 420P; Mitsui Chemicals Inc.)
- c. Low-density oxidation-type polyethylene wax  
(AC-629: Allied Chemical)
- d. Zinc stearate
- e. Pentaerythritol adipate-stearate high-molecular-weight ester wax  
(Rikemal EW-200; Riken Vitamin)
- f. Acrylic-acid polymer-type lubricant  
(Metablen L-1000: Mitsubishi Rayon Co., Ltd.)

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contradictory. By contrast, the reference to the upper end of the range that appears later in this sentence unambiguously indicates "greater than", and not "equal to or greater than."]

**[0015]** The evaluation results displayed in the table are categorized as described hereunder.

**Evaluation**

**Transparency:**

- 1: exceptional
- 2: good
- 3: fair
- 4: poor

**Release lubricity:**

- 1: exceptional
- 2: good
- 3: slightly sticky
- 4: sticky

**Plate-out:**

- 1: none at all
- 2: rolls became appreciably cloudy
- 3: rolls became completely cloudy

**[0016]**

**[Table 1]**

	Transparency	Gelling time (min)	Release lubricity	Sticking time (min)	Plate-out characteristics
Synthesis Product 1	1	1.5	1	>30	1
Synthesis Product 2	2	2.0	1	>30	1
Synthesis Product 3	1	1.0	2	20	1
Synthesis Product 4	1	1.0	2	15	1
Synthesis Product 5	1	1.0	2	15	1
Example 6	1	1.0	1	>30	1
Comparative Example a	2	1.0	4	0	1
Comparative Example b	3	3.0	4	0	1
Comparative Example c	3	3.5	2	20	3
Comparative Example d	3	2.0	4	0	1
Comparative Example e	4	4.5	3	10	2
Comparative Example f	2	1.0	3	5	2

[0017]

**[Effect of the Invention]** As has been described in the foregoing, 0.01 to 5.0 wt parts of the aforementioned compound of General Formula (I) was compounded with 100 wt parts of an amorphous random copolyester resin, which resulted in an exceptional effect whereby the resulting amorphous random polyester resin composition exhibits exceptional calenderability while having undiminished gelling and transparency characteristics, a lubricity that does not result in plate-out during molding, and improved blooming/bleeding characteristics over time.

(72) Inventor: Masao SASAKI c/o Okamoto Industries Incorporated 1 Kando, Yoshida-cho, Haibara-gun Shizuoka Prefecture	(72) Inventor: Susumu ASAO c/o Daikyo Kasei Kogyo Co., Ltd. 23-27 Toneri 5-chome, Adachi-ku, Tokyo
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